

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



# PATENT SPECIFICATION

(11) 1 209 590

1 209 590

NO DRAWINGS

- (21) Application No. 22592/69 (22) Filed 2 May 1969  
 (31) Convention Application No. P 17 71 312.1  
 (32) Filed 4 May 1968 in  
 (33) Germany (DT)  
 (45) Complete Specification published 21 Oct. 1970  
 (51) International Classification C 03 c 3/08  
 (52) Index at acceptance

C1M 11B1 11C11 11C12 11C3 11C5 11C7 11C8  
 11C9 11F1 11F10 11F15 11F2 11F20 11F24  
 11F3 11F30 11F33 11F4 11F5 11J2 11J3 11K1  
 11K5 11K9



## (54) IMPROVEMENTS IN OR RELATING TO GLASS

(71) We, CARL-ZEISS-STIFTUNG, a Foundation established under the laws of Germany, of Heidenheim a.d. Brenz, Wurttemberg, Germany, trading as JENAER GLASWERK SCHOTT & GEN., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—  
 The present invention relates to a fluorine-containing borosilicate glass.  
 It is known that wave fronts are deformed in a glass when the optical path length is of different value at different parts of the glass because of temperature gradients which occur.  
 Optical instruments in space vehicles are exposed to strong temperature differences for example, due to temporary exposure to solar

radiation and due to subsequent radiation into space, and also by emitted and/or reflected infra-red rays from close planets. These temperature differences can cause wave deformations in the optical glasses, and such waves considerably reduce the resolving power of the optical systems.

Also in connection with aerial photography, for example, the temperature gradients which are established can considerably reduce the resolution. Accordingly, there is a great demand for optical systems and optical sealing windows consisting of glasses with an optical path length not dependent on temperature.

With planoparallel sealing windows, for example, the change in optical path length resulting from the change in temperature is

$$\Delta W = W_1 - W_2 = d \cdot G \cdot \Delta t = d \cdot \left\{ \alpha (n-1) + \frac{dn}{dt} \right\} \cdot \Delta t$$

A disturbing wave deformation is caused when  $\Delta W$  is of different value at different places of the sealing window because of temperature gradients which are set up.  $W$  is the optical wavelength,  $t$  is the temperature and  $n$  is the refractive index. The equation shows that the optical path difference  $\Delta W$  can be decreased by reducing the thickness  $d$  of the glass element, the temperature difference  $\Delta t$

or the value  $G = (n-1)\alpha + \frac{dn}{dt}$ . The expansion coefficient is denoted by  $\alpha$ . The value  $G$  only depends on the physical properties of the glass and should be as small as possible, being 0 in the ideal case. The value  $G$  is a characteristic value defined in terms of refractive index, expansion coefficient and rate of change of refractive index with temperature. The value must therefore be negative. This seems

possible by the introduction of glass components

- 1) which cause the best possible increase in the coefficient of thermal expansion,
- 2a) which so influence the glass that the dependence on temperature of the ultra-violet characteristic frequency

$$\left[ \frac{d\lambda_0}{dt} \right]$$

- remains as small as possible, and/or
- 2b) which produce a displacement of the ultra-violet characteristic frequencies  $\lambda_0$  of the glass towards small wavelengths.

However, the increase in the thermal expansion which is necessary according to 1) makes it difficult to maintain the condition

$G=0$ , since the temperature coefficient  $\frac{dn}{dt}$  must assume very high negative values on account of the resultant raising of the term

Striker in P 2077 GB

(n-1). a. This contrast clearly shows the difficulties which exist when developing glasses with an optical path length not dependant on temperature.

on the image-forming properties is substantially excluded.

According to this invention we provide a fluorine-containing borosilicate glass consisting of the following constituents expressed as weight percentages: 10

5 It is thus the object of the present invention to provide a glass with which the disturbing influence of a temperature gradient

|        |   |          |
|--------|---|----------|
| (i)    | SiO <sub>2</sub>                                      | 14 — 63  |
| (ii)   | B <sub>2</sub> O <sub>3</sub>                         | 6 — 20   |
| (iii)  | Al <sub>2</sub> O <sub>3</sub>                        | 5 — 18   |
| (iv)   | Alkali metal oxide(s) and/or alkali metal fluoride(s) | 8 — 20.2 |
| (v)    | Sb <sub>2</sub> O <sub>3</sub>                        | 1.5 — 32 |
| (vi)   | F other than that contained in (iv)                   | 1 — 12   |
| (vii)  | ZnO   | 0 — 2    |
| (viii) | CdO   | 0 — 2    |
| (ix)   | GeO <sub>2</sub>                                      | 0 — 10   |
| (x)    | WO <sub>3</sub>                                       | 0 — 3    |
| (xi)   | Ta <sub>2</sub> O <sub>5</sub>                        | 0 — 4    |
| (xii)  | Nb <sub>2</sub> O <sub>5</sub>                        | 0 — 15   |
| (xiii) | Bi <sub>2</sub> O <sub>3</sub>                        | 0 — 15   |
| (xiv)  | SO <sub>4</sub> —                                     | 0 — 8    |
| (xv)   | As <sub>2</sub> O <sub>3</sub>                        | 0 — 5    |
| (xvi)  | PbO   | 0 — 10   |
| (xvii) | Alkaline earth metal oxide(s)                         | 0 — 1    |

Item (iv) may be chosen from the following components expressed as weight percentages:

|                   |        |
|-------------------|--------|
| K <sub>2</sub> O  | 0 — 18 |
| Na <sub>2</sub> O | 0 — 14 |
| Rb <sub>2</sub> O | 0 — 5  |
| Cs <sub>2</sub> O | 0 — 5  |
| Li <sub>2</sub> O | 0 — 5  |
| KF                | 0 — 18 |

Preferably item (iv) is K<sub>2</sub>O and/or KF. Expediently at least 40% of the glass is represented by items (i), (ii) and (iii).

5 Fluorine can be supplied as fluoride (e.g. KF,  $\text{AlF}_3$ ), as difluoride (e.g.  $\text{KHF}_2$ ) or in other form (e.g. as silicofluoride) to the melt. The  $n$  values of the glasses according to the invention are generally greater than 1.44 and the  $\gamma_d$  values are generally less than 70.

10 By introducing up to 8% by weight of  $\text{SO}_4^{--}$  (e.g. as  $\text{Al}_2(\text{SO}_4)_3$ ), a strong increase in the viscosity is caused and it has additional influence on the main and partial dispersions of the glass.

15 In glasses having a basis of  $\text{SiO}_2$ , the glass components fluorine,  $\text{B}_2\text{O}_3$  and  $\text{K}_2\text{O}$  shift the  $\frac{dn}{dt}$  values in a negative direction, without

substantially increasing the thermal expansion.

The fluorine component also has the effect that the independance of the ultra-violet char-

acteristic frequency  $\frac{d\lambda_0}{dt}$  on temperature re- 20

mains as small as possible. Increasing  $\text{B}_2\text{O}_3$  content displaces the ultra-violet characteristic frequency  $\lambda_0$  towards short wavelengths, and  $\text{Sb}_2\text{O}_3$  does not unfavourably change the ultra-violet characteristic frequency  $\lambda_0$ . 25

Examples of compositions expressed as weight percentages of the glasses embodying this invention are given with their physical properties in the following Table.

|   | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      |
|---|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO <sub>2</sub>                                | 48.9   | 49.8   | 44.5   | 41.5   | 37.3   | 38.1   | 36.5   | 37.0   |
| B <sub>2</sub> O <sub>3</sub>                   | 14.9   | 17.2   | 17.8   | 15.2   | 15.3   | 17.7   | 13.2   | 9.6    |
| Al <sub>2</sub> O <sub>3</sub>                  | 6.5    | 7.1    | 14.3   | 15.2   | 13.7   | 14.4   | 12.8   | 11.5   |
| Li <sub>2</sub> O                               |        |        |        |        |        |        |        |        |
| Na <sub>2</sub> O                               | 0.1    | 0.3    | 1.4    | 0.3    | 0.3    | 0.5    | 0.1    | 2.0    |
| K <sub>2</sub> O                                | 6.2    | 6.3    | 3.5    | 3.3    | 3.0    | 3.1    | 2.9    | 12.5   |
| Sb <sub>2</sub> O <sub>3</sub>                  | 9.8    | 4.7    | 4.7    | 4.7    | 14.6   | 9.5    | 19.7   | 13.8   |
| KF  | 12.5   | 13.4   | 12.6   | 16.6   | 13.7   | 14.6   | 12.9   |        |
| AlF <sub>3</sub>                                | 0.8    | 0.9    | 0.9    | 2.9    | 1.8    | 1.8    | 1.6    | 13.3   |
| WO <sub>3</sub>                                 |        |        |        |        |        |        |        |        |
| Nb <sub>2</sub> O <sub>5</sub>                  |        |        |        |        |        |        |        |        |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> |        |        |        |        |        |        |        |        |
| PbO   |        |        |        |        |        |        |        |        |
| As <sub>2</sub> O <sub>3</sub>                  | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    |
| F <sup>-</sup>                                  | 4.3    | 4.5    | 4.2    | 5.6    | 4.5    | 4.8    | 4.3    | 3.8    |
| SO <sub>4</sub> <sup>2-</sup>                   |        |        |        |        |        |        |        |        |
| n <sub>d</sub>                                  | 1.4924 | 1.4822 | 1.4710 | 1.4619 | 1.4875 | 1.4718 | 1.4952 | 1.4799 |
| d   | 61.1   | 64.5   | 62.2   | 63.0   | 55.1   | 58.9   | 51.9   | 55.8   |
| α.10 <sup>-7</sup> /°C                          |        | 95     | 90     | 108    | 100    | 104    | 96     |        |
| Δn  |        |        |        |        |        |        |        |        |
| — abs. * (20—40°C)                              |        | —3.3   | —4.3   | —4.8,  | —4.5   | —4.6   | —4.7   |        |
| Δ+  |        |        |        |        |        |        |        |        |
| for + 546.1                                     |        |        |        |        |        |        |        |        |
| G abs.+(H—I) α + $\frac{\Delta n}{\Delta t}$    | +1.4   | +1.3   | —0.1   | +0.2   | —0.4   | +0.3   | +0.5   |        |

\* Change in refractive index with respect to vacuum.

|   | 9      | 10     | 11     | 12     | 13     | 14     | 15     | 16     | 17     |
|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO <sub>2</sub>                                | 36.2   | 34.0   | 34.8   | 29.2   | 38.3   | 35.4   | 34.6   | 25.1   | 15.8   |
| B <sub>2</sub> O <sub>3</sub>                   | 7.2    | 8.7    | 16.9   | 11.0   | 11.0   | 10.2   | 10.3   | 17.4   | 15.1   |
| Al <sub>2</sub> O <sub>3</sub>                  | 11.2   | 9.2    | 9.8    | 10.8   | 12.3   | 11.4   | 11.4   | 14.3   | 14.3   |
| Li <sub>2</sub> O                               |        |        |        |        |        |        |        |        | 0.3    |
| Na <sub>2</sub> O                               | 12.5   | —      | 3.5    | 0.1    | 0.1    | 0.1    | 0.1    | 0.5    | 0.5    |
| K <sub>2</sub> O                                | —      | 11.0   | 10.9   | 1.2    | 8.7    | 8.1    | 8.1    | 1.5    | 1.5    |
| Sb <sub>2</sub> O <sub>3</sub>                  | 10.0   | 22.2   | 9.5    | 16.5   | 19.5   | 25.2   | 25.3   | 18.8   | 30.4   |
| KF  |        | 3.1    |        | 13.9   | 7.3    | 6.9    | 6.6    | 15.8   | 15.8   |
| AlF <sub>3</sub>                                | 18.3   | 11.5   | 14.3   | 1.4    | 1.9    | 1.8    | 1.5    | 6.0    | 6.0    |
| WO <sub>3</sub>                                 |        |        |        |        | 0.1    | 0.1    | 0.5    |        |        |
| Na <sub>2</sub> O <sub>5</sub>                  |        |        |        |        |        |        | 1.1    |        |        |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> |        |        |        | 15.6   |        |        |        |        |        |
| PbO   | 4.3    |        |        |        | 0.5    | 0.5    | 0.4    |        |        |
| As <sub>2</sub> S <sub>3</sub>                  | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    | 0.3    |
| F <sup>-</sup>                                  |        | 1.2    |        | 4.8    | 2.5    | 2.5    | 2.5    | 5.5    | 5.5    |
| SO <sub>4</sub> <sup>2-</sup>                   |        |        | 6.0    |        |        |        |        |        |        |
| <i>n<sub>d</sub></i>                            | 1.4978 | 1.5045 | 1.4957 | 1.5068 | 1.5111 | 1.5262 | 1.5334 | 1.4930 | 1.5142 |
| <i>d</i>  | 53.4   | 49.8   | 56.0   | 50.9   | 50.6   | 47.0   | 45.4   | 51.5   | 44.7   |

PRODUCTION EXAMPLE:

5 A batch consisting of 750 kg. of silicon di-  
oxide, 460 kg. of boron oxide, 145 kg. of  
aluminium hydroxide, 8 kg. of sodium  
carbonate, 140 kg. of potassium car-  
bonate, 71 kg. of antimony tri-  
oxide, 201 kg. of potassium fluoride, 13.5 kg.  
of aluminium fluoride and 4.5 kg. of arsenic  
trioxide is thoroughly mixed in a commercial  
10 mixer. After introduction and complete melt-  
ing of the bath in a ceramic basin at 1380°C.,  
for which about 12 hours are required, the  
melt is refined for 8 hours at 1400°C. The  
furnace temperature is thereafter allowed to

fall while stirring constantly until the glass 15  
has assumed the viscosity of about 400 poises  
which is suitable for pouring. The glass is  
then poured into a preheated iron mould and  
then cooled to room temperature. A glass is  
obtained which corresponds to Example 2 in 20  
the Table. The cooling from the transforma-  
tion point  $T_g$  (360°C.) down to room tem-  
perature is a 1°C./hour, i.e. takes about 14  
days.

WHAT WE CLAIM IS:—

1. A fluorine-containing borosilicate glass 25  
consisting of the following constituents ex-  
pressed as weight percentage:

|        |  |          |
|--------|--|----------|
| (i)    | SiO <sub>2</sub>   | 14 — 63  |
| (ii)   | B <sub>2</sub> O <sub>3</sub>                            | 6 — 20   |
| (iii)  | Al <sub>2</sub> O <sub>3</sub>                           | 5 — 18   |
| (iv)   | Alkali metal oxide(s) and/or<br>alkali metal fluoride(s) | 8 — 20.2 |
| (v)    | Sb <sub>2</sub> O <sub>3</sub>                           | 1.5 — 32 |
| (vi)   | F other than that contained in (iv)                      | 1 — 12   |
| (vii)  | ZnO  | 0 — 2    |
| (viii) | CdO  | 0 — 2    |
| (ix)   | GeO <sub>2</sub>   | 0 — 10   |
| (x)    | WO <sub>3</sub>  | 0 — 3    |
| (xi)   | Ta <sub>2</sub> O <sub>5</sub>                           | 0 — 4    |
| (xii)  | Nb <sub>2</sub> O <sub>5</sub>                           | 0 — 15   |
| (xiii) | Bi <sub>2</sub> O <sub>3</sub>                           | 0 — 15   |
| (xiv)  | SO <sub>3</sub>  | 0 — 8    |
| (xv)   | As <sub>2</sub> O <sub>3</sub>                           | 0 — 5    |
| (xvi)  | PbO  | 0 — 10   |
| (xvii) | Alkaline earth metal oxide(s)                            | 0 — 1    |



2. A glass according to Claim 1, wherein item (iv) is chosen from the following components expressed as weight percentages:

|         |        |
|---------|--------|
| $K_2O$  | 0 — 18 |
| $Na_2O$ | 0 — 14 |
| $Rb_2O$ | 0 — 5  |
| $Cs_2O$ | 0 — 5  |
| $Li_2O$ | 0 — 5  |
| KF      | 0 — 18 |

3. A glass according to Claim 1, wherein  
5 item (iv) is  $K_2O$  and/or KF.

4. A glass according to any preceding claim,  
wherein at least 40% by weight of the glass is  
represented by items (i), (ii) and (iii).

5. A glass substantially as herein described  
10 and exemplified.

MEWBURN ELLIS & CO.,  
Chartered Patent Agents,  
70—72 Chancery Lane,  
London, W.C.2.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

**THIS PAGE BLANK (USPTO)**